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(54) **BF3 removal from olefin oligomerisation product stream and recycling of the recovered BF3**

BF3-Rückgewinnung aus Olefinoligomerisierungsprodukten und Rückführung des rückgewonnenen BF3

Récupération de BF3 à partir d'un produit de l'oligomérisation d'oléfines et recyclage du BF3 récupéré

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(73) Proprietor: **AMOCO CORPORATION**
Chicago Illinois 60680-0703 (US)

(72) Inventor: **Presedo, Hector**
Baton Rouge, Louisiana 70816 (US)

(74) Representative:
Ritter, Stephen David et al
Mathys & Squire
100 Grays Inn Road
London WC1X 8AL (GB)

(56) References cited:
EP-A- 0 364 889 **EP-A- 0 493 024**
EP-A- 0 594 065 **US-A- 4 238 417**
US-A- 4 282 013

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Description

[0001] Alpha-olefin oligomers and their use as hydraulic fluids and synthetic lubricants (synlubes) are well known. U.S. Patent No. 2,927,129 reports the oligomerization of C_{5-14} α -olefins using a dialkyl peroxide catalyst to make a synlube. U.S. Patent No. 3,113,167 describes an α -olefin oligomer process using a titanium halide and an aluminum compound as the oligomerization catalyst.

[0002] The preferred catalysts for making α -olefin oligomers are Friedel-Crafts catalysts such as boron trifluoride (BF_3) as disclosed in U.S. Patent No. 3,149,178. Optimum properties are obtained starting with 1-decene although mixtures of α -olefins have been used, cf. U.S. Patent No. 3,330,833.

[0003] The preferred Friedel-Crafts catalyst is BF_3 . Pure BF_3 is not an effective oligomerization catalyst. A small amount of polar compound is necessary as a promoter which forms a complex with the BF_3 . U.S. Patent No. 3,382,291 describes the use of alcohol promoters such as decanol. Other reported promoters are mordenite (hydrogen form), water, phosphoric acid, fatty acids (e.g., valeric acid), ketones, organic esters, ethers, polyhydric alcohols, silica gel and the like.

[0004] While the BF_3 based catalysts are preferred, they are expensive and, in many cases, not easily reused and must be disposed of, which in itself presents a significant problem. Thus, it would be beneficial to be able to recover BF_3 values in a manner which would allow for catalyst recycle.

[0005] The product stream from the olefin oligomerization is a liquid and contains a mixture of α -olefin oligomers, dissolved BF_3 and the BF_3 and promoter complex. The dissolved BF_3 is not present in a great amount but can be recovered by any of several different recovery methods. Vogel, et al., U.S. Patent No. 4,454,366 and U.S. Patent No. 4,384,162, describe the use of polyvinyl alcohol to remove BF_3 from an oligomerization reaction. Vogel, et al., U.S. Patent No. 4,433,197, contacts the reaction product with silica to remove the BF_3 . Morganson, et al., U.S. Patent No. 4,429,177, and Madgavkar, et al., U.S. Patent No. 4,213,001 and U.S. Patent No. 4,308,414, use silica as an absorbent for BF_3 in an oligomerization process. Madgavkar, et al., U.S. Patent No. 4,394,296, describe the use of wet silica as a co-catalyst with BF_3 in an oligomer process. The silica can be filtered off and recycled as the catalyst. Madgavkar, et al., U.S. Patent No. 4,263,467, remove BF_3 by trickling the reaction product over an inert metallic or ceramic bed whereby the BF_3 is said to evaporate and can be recovered. Tyser, et al., U.S. 4,981,578, teaches the recovery of BF_3 by contacting the oligomer product stream with solid or aqueous KF, NaF or NH_4F . Walker, et al., U.S. 4,956,513, teaches BF_3 recovery by extracting BF_3 from the oligomer reaction product by washing same with water.

[0006] EP 0 594 065 describes a process for recover-

ing BF_3 from an oligomerization mixture using a copper-nickel-made recovery reactor and heating the oligomerization mixture at or above a decomposition temperature of the BF_3 and cocatalyst complex. EP 0 364 889 describes a process for the manufacture of olefin oligomer which includes removal of BF_3 or BF_3 -alcohol complex. The BF_3 gas is removed from the oligomerization mixture by evacuation, blowing an inert gas into the product or heating at relatively elevated temperature.

[0007] From the above it can be seen that a great deal of effort has gone into developing a method for removing BF_3 from an olefin oligomerization process in an environmentally safe manner.

[0008] According to the present invention, there is provided a process for recovering BF_3 from a BF_3 /promoter complex catalyzed olefin oligomerization product stream, which process comprises:

(a) thermally cracking at least a portion of the complex in the product stream to yield gaseous BF_3 , wherein said cracking is conducted at a temperature below 80 °C;

(b) contacting gaseous BF_3 from (a) with a liquid olefin stream having a temperature within the range of from 0 to 40 °C, the liquid olefin stream containing from 0.05 to 1.5 wt% promoter; and

(c) passing the resulting olefin stream containing the dissolved BF_3 and BF_3 /promoter complex to an oligomerization reactor unit.

[0009] In more detail, this invention relates to a process for the recovery of BF_3 from a promoted BF_3 catalyzed olefin oligomerization product stream. The recovered BF_3 can come from that which is dissolved in the liquid product stream and that which is present as a BF_3 /promoter complex. The process features the thermal cracking of at least a portion of the BF_3 /promoter complex to yield promoter and gaseous BF_3 . The BF_3 gas is effervescent to the extent that it is not dissolved in the stream. With regard to the dissolved BF_3 , be it from thermal cracking or otherwise, its concentration in the stream will be attenuated as the thermal cracking heats the stream to thereby increase the vapor pressure of the dissolved BF_3 so that at least a portion thereof leaves the stream as a gas.

[0010] The gaseous BF_3 is recoverable for reuse by contacting (e.g. quenching) the gas with a liquid olefin stream (as specified in (b) above). Preferably, the olefin stream will be the same as that used to feed the oligomerization reaction. The quenching results in a portion of the gaseous BF_3 being dissolved in the stream. In the absence of a promoter, the benefits from such a quenching are limited by the solubility of the BF_3 in the olefin stream. It is well recognized that such solubility is rather small. As a result, not much of the gaseous BF_3 would be recovered in this manner.

[0011] Instead, in accordance with the invention, the gaseous BF_3 is contacted with a liquid olefin stream

which contains a promoter. With this technique, there is obtained a much greater BF_3 presence in the stream. The promoter forms a complex with the BF_3 , which complex can be present in the olefin stream in an amount which is much greater than that which can be obtained by simply dissolving BF_3 in the stream. Thus, much of the gaseous BF_3 can be reused and there can be obtained an α -olefin stream which contains dissolved BF_3 and the BF_3 /promoter complex and which, as a result, is suitable for feed to an olefin oligomerization reaction.

Description of the Drawing

[0012] Figure 1 is a schematic diagram depicting a process of this invention.

Detailed Description of the Invention

[0013] Methods of conducting a BF_3 catalyzed oligomerization process are well-known. In one mode, BF_3 is merely bubbled through the α -olefin reaction mixture containing a promoter during the oligomerization. In a preferred mode, the process is conducted under BF_3 pressure. A useful pressure is about 6.89 - 689 kPa (1-100 psig), preferably 34.5 - 344.5 kPa (5-50 psig) more preferably about 68.9 - 137.8 kPa (10-20 psig).

[0014] Any of the known promoters for BF_3 can be used such as water, alcohol (e.g., methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, n-hexanol, 2-ethyl hexanol, n-decanol, n-dodecanol and the like, including mixtures thereof), fatty acids (e.g., valeric, caproic and the like), organic esters (e.g., butyl acetate, methyl valerate, ethyl octanoate, and the like), ketones (e.g., methyl ethyl ketone, methyl isobutyl ketone, and the like), ethers (e.g., dibutyl ether, tetrahydrofuran, dioxane and the like), alkoxyated alcohols (e.g., 2-ethoxyethanol and the like), polyhydric alcohols (e.g., glycol, glycerol, and the like), inorganic acids (e.g., phosphoric and the like), silica, zeolites and the like.

[0015] The preferred promoters are water and alcohols containing 1-8 carbon atoms, such as methanol, ethanol, isopropanol, n-propanol, n-butanol, isobutanol, n-hexanol and n-octanol. The more preferred promoters are alcohols containing 2-5 carbon atoms. The most preferred promoters are n-propanol and n-butanol.

[0016] The amount of promoter should be an amount that causes the BF_3 to act as an oligomerization catalyst. This is referred to as a promoter amount. A useful range is 0.1-2.0 weight percent of the α -olefin.

[0017] Alpha-olefins useful in the process are those containing 6 to 36 and, preferably, 8 to 12 carbon atoms such as 1-octene, 1-decene, 1-dodecene and the like, including mixtures thereof. The most preferred α -olefin is 1-decene or an olefin mixture containing mainly, for example, at least 75 weight percent 1-decene.

[0018] The cold liquid olefin stream is preferably at least similar if not identical in constituents and amounts

as is specified for the olefin feed stream for the oligomerization reactor.

[0019] Even though α -olefins are the main focus of the processes of this invention, it is to be understood that these same processes are likewise applicable to product streams which contain dissolved BF_3 and BF_3 /promoter complex and which are principally a mix of α -olefin and internal olefin or principally internal olefin. Suitable internal olefins are linear or branched and contain 6 to 36 carbon atoms. The internal olefin is a mix of olefin isomers with the double bond being located in various non- α positions.

[0020] The preferred reaction temperature is 20-50°C and more preferably 25-40°C. Superior results have been achieved at about 30°C. Lower temperatures will increase the amount of higher oligomers but at the cost of a slower reaction rate. High temperatures give a fast reaction rate but increased yield of dimer.

[0021] The amount of BF_3 in the reaction mixture should be in excess of the amount required to complex with the promoter. This can be accomplished by saturating the reaction mixture with BF_3 such as by continuously bubbling BF_3 through the reaction mixture. More preferably, the reaction is conducted in a closed vessel under BF_3 pressure. A useful pressure range is 6.89-689 kPa (1-100 psig) to about 34.45-344.5 kPa (5-50 psig) and most preferably 68.9-137.8 kPa (10-20 psig).

[0022] The oligomerization is usually conducted until the monomer content of the reaction mixture drops below 5 weight percent, more preferably below 2 weight percent. After the oligomerization reaction has proceeded to the desired extent, the reactor contents, which include the produced oligomer mix, dissolved BF_3 and BF_3 /promoter complex, are removed for treatment in accordance with the instant invention.

[0023] The removed contents, which can also be denominated as the α -olefin oligomerization product stream, will have a temperature no higher than about 50°C, and most usually from 25 to 35°C. To effect the thermal cracking of the contained BF_3 /promoter complex, the removed product stream is to be heated to the cracking temperature. It is important that the cracking temperature not be significantly exceeded as excessive temperatures can adversely affect the product stream. Thus, in accordance with the invention the cracking temperature does not exceed 80°C, and most preferably is within the range of from 50 to 75°C. The cracking temperature, of course, depends on the thermal stability of the complex used. Thus, it is preferred that the complex chosen be one which gives good catalytic activity but which has an acceptably low cracking temperature. The alcohol promoters, especially n-butanol and n-propanol, are most suitable in this regard.

[0024] The α -olefin oligomerization product stream can be heated in any conventional manner, for example, it can be passed through a tube and shell heat exchanger or contacted with a hot, inert heating medium such as N_2 . It is preferred to use the latter at

least at the point where there is a presence of gaseous BF_3 as the inert medium can then also act as a stripping medium. When the medium is a gas, however, there will be required a high volume of gas to raise the product stream temperature all the way to the cracking temperature due to the gas' low heat capacity as compared to that of the product stream. Therefore, it is preferred that the product stream be heated by efficient means, e.g., a heat exchanger, to a temperature which is near or at the cracking temperature and then contacting the product stream with a hot gaseous heating/stripping medium. For example, a conventional heat exchanger can be used to raise the product stream temperature to, say, 40-65°C. Then, the hot product stream can be contacted with a hot gaseous medium to, as the case may be, either (1) raise the product stream temperature to the needed cracking temperature and effect BF_3 stripping or (2) to effect BF_3 stripping and to hold the product stream at the cracking temperature. For n-butanol and n-propanol, the cracking temperature will be within the range of from 50 to 65°C.

[0025] The preferred gaseous heating/stripping medium is N_2 , CH_4 , C_2H_6 , and CO_2 . Preferred are N_2 and CH_4 , with N_2 being most preferred. Again, due to the low heat capacity of the gaseous medium, its temperature can be in excess of the cracking temperature provided that such a temperature does not cause significant thermal degradation of product stream constituents, especially the oligomers and/or promoters. When N_2 is the medium, an N_2 temperature range of from 50 to 200°C and, most preferably within the range of from 75 to 150°C can be used. The same can be said for any other suitable medium having a heat capacity similar to that of N_2 .

[0026] To insure high efficiency and economy, it is preferred that the preheated product stream be contacted with the hot gaseous medium in a stripping column in a counter-current manner. The product stream can be fed to the column at a point which is above the feed point for the gaseous medium feed. To enhance the contact between the two phases and to aid the stripping function, the stripping column can be provided with conventional internals, such as packing or trays. The heating/stripping medium, BF_3 , promoter and some olefin will leave the upper portion of the stripping column as a gas, while a refined, α -olefin oligomerization product will leave the lower portion of the column as a liquid.

[0027] Depending on the identity of the promoter and olefin in the original product stream and the stripping gas used, it may be beneficial to operate the stripping column under atmospheric pressure or under a moderate vacuum, say 34.5 - 68.9 kPa (5 to 10 psia).

[0028] The gas from the thermal cracking step is next treated to recover its BF_3 constituent. A most beneficial recovery technique is to contact the gas with a cold, liquid olefin stream which contains promoter. Should there be no promoter present, then the BF_3 carrying capacity of the olefin stream will be limited to that amount of BF_3

which is dissolved into the stream. With an adequate amount of promoter in the olefin stream, the BF_3 (as the BF_3 /promoter complex) carrying capacity of the olefin stream can be sufficient in that the stream can be fed directly to the original oligomerization reaction. The preferred amount of promoter is the same amount as that mentioned in the discussion of the oligomerization reaction.

[0029] Note that some promoter can be provided to the liquid olefin stream by the gas stream from the thermal cracking step. The amount of promoter present in the gas from the thermal cracking step depends on the operating temperature and pressure of the stripping column. Thus, the amount of promoter which needs to be in the cold olefin stream prior to its contact with the thermal cracking gas is at least the difference between the amount of promoter needed for the olefin oligomerization feed stream and the amount which is provided by the thermal cracking gas.

[0030] The foregoing, which concerns the amount of promoter needed, pre-supposes that there will be an adequate amount of BF_3 available to provide for the complex and dissolved BF_3 levels needed for a suitable olefin feed stream. If there is an insufficient amount of BF_3 in the thermal cracking gas, then the amount of promoter needed in the cold olefin stream can be likewise reduced if desired, or, preferentially, additional BF_3 can be added to the complex with the excess promoter prior to the oligomerization reactor.

[0031] Generally, a suitable amount of promoter in the cold olefin stream is within the range of from 0.05 to 1.5 wt% and, preferably, within the range of from 0.15 to 1.0 wt%. The weight percentages being based on the weight of the olefin.

[0032] The contact between the cold olefin stream and the thermal cracking gas can be accomplished in an absorber/direct-contact condensation column. This column preferably has internals, such as trays or packing, to enhance contact between the two phases. Preferably, the cold olefin stream is at a temperature within the range of from 0 to 50°C and, most preferably, within the range of from 15 to 35°C. The column operates at a pressure within the range of from 13.8-138 kPa (2 to 20 psia), and preferentially, within the range of 34.5-103 kPa (5 psia to 15 psia). The gaseous stream leaving the upper portion of this column will contain mainly nitrogen and a small amount of BF_3 . From the lower portion of the column will exit a liquid olefin stream containing dissolved BF_3 and BF_3 /promoter complex.

[0033] There are other apparatuses in which the absorption/condensation step can occur. A particularly preferred apparatus is a liquid ring vacuum pump, which is also known as a liquid piston vacuum pump. The thermal cracking gas is sent to the intake side of the pump, with the cold olefin being fed to act as the liquid ring or piston. Discharged from the pump is a liquid gas mix which can be sent to a knock-out drum for separation. This type of pump is advantageous because it

enhances the mixing and contact between the cold olefin and the thermal cracking gas and because it can be used to apply the optional vacuum to the apparatus, e.g., stripping column, to which the olefin oligomerization product stream and heating/stripping medium are fed. The discharge side of the pump is preferably at superatmospheric pressure.

[0034] Referring now to Figure 1, there can be seen a schematic depiction of a process of this invention. The temperatures, pressures, concentrations, promoter identity; and other process parameters discussed previously all apply to the depicted process and, for the sake of brevity, will not be repeated.

[0035] A liquid α -olefin oligomerization product stream is first fed via line 1 to heater 5, which raises the oligomer temperature, and then, is fed via line 2 to thermal cracking/stripping packed column 8. This feed occurs above a hot N_2 feed, via line 4, to the same column. In line 4 is N_2 heater 6 which raises the N_2 (including recycled N_2) temperature to the level described earlier. The flow in packed column 8 is counter current flow. Withdrawn from packed column 8, via line 12, is poly α -olefin oligomer having a greatly reduced BF_3 content. Exiting the upper portion of packed column 8 is a gas comprised of N_2 , BF_3 and some promoter. The gas is conveyed via line 10 to liquid ring vacuum pump 16. Also fed to vacuum pump 16 via line 14 is cool liquid α -olefin and promoter. By way of vacuum pump 16 and line 10 a sub-atmospheric pressure can be maintained in packed column 8, if desired. Vacuum pump 16 discharges, generally at super-atmospheric pressure, a liquid-gas mix which is conveyed via line 18 to liquid/gas separator drum 20. N_2 and some BF_3 and promoter are vented via line 22 from drum 20 as a gas. A small fraction of this stream may be vented to a scrubber to purge impurities if required, via line 26. Most of the gas is recycled via line 22, back to line 4. From the lower portion of drum 20 is withdrawn, via line 24, a liquid α -olefin stream which contains dissolved BF_3 and BF_3 /promoter complex. This liquid olefin stream can be sent to the oligomerization reactor unit.

Claims

1. A process for recovering BF_3 from a BF_3 /promoter complex catalyzed olefin oligomerization product stream, which process comprises:

- (a) thermally cracking at least a portion of the complex in the product stream to yield gaseous BF_3 , wherein said cracking is conducted at a temperature below 80 °C;
- (b) contacting gaseous BF_3 from (a) with a liquid olefin stream having a temperature within the range of from 0 to 40 °C, the liquid olefin stream containing from 0.05 to 1.5 wt% promoter; and
- (c) passing the resulting olefin stream contain-

ing the dissolved BF_3 and BF_3 /promoter complex to an oligomerization reactor unit.

2. The process of Claim 1 wherein the olefin stream in (b) is selected from the group consisting of α -olefin, internal olefin or a mixture thereof.
3. The process of Claim 2 wherein the α -olefin contains 6 to 36 carbon atoms and wherein the internal olefin contains 6 to 36 carbon atoms.
4. The process of Claim 1 wherein the liquid olefin stream in (b) is at least predominately 1-decene.
5. The process of any of Claims 1-4 wherein the promoter portion of the complex thermally cracked in (a) is an alkanol containing 1-8 carbon atoms.
6. The process of any of Claims 1-5 wherein the alkanol is n-butanol or n-propanol.
7. The process of any of Claims 1-6 wherein the promoter in the liquid olefin in (b) is the same as the promoter in the thermally cracked complex.

Patentansprüche

1. Verfahren zur Rückgewinnung von BF_3 aus einem Produktstrom einer mit einem BF_3 /Promotor-Komplex katalysierten Olefin-Oligomerisation, welches Verfahren umfaßt:

(a) thermisches Cracken von mindestens einem Teil des Komplexes in dem Produktstrom, um gasförmiges BF_3 zu erhalten, wobei das Cracken bei einer Temperatur von weniger als 80°C durchgeführt wird;

(b) In-Kontakt-Bringen des gasförmigen BF_3 aus (a) mit einem flüssigen Olefinstrom mit einer Temperatur innerhalb des Bereichs von 0 bis 40°C, wobei der flüssige Olefinstrom von 0,05 bis 1,5 Gew.-% eines Promotors enthält; und

(c) Leiten des resultierenden Olefinstroms, der das gelöste BF_3 und einen BF_3 /Promotor-Komplex enthält, zu einer Oligomerisationsreaktor-einheit.

2. Verfahren nach Anspruch 1, wobei der Olefinstrom in (b) aus der Gruppe ausgewählt ist bestehend aus α -Olefin, innerem Olefin oder einer Mischung davon.
3. Verfahren nach Anspruch 2, wobei das α -Olefin 6 bis 36 Kohlenstoffatome enthält und wobei das innere Olefin 6 bis 36 Kohlenstoffatome enthält.

4. Verfahren nach Anspruch 1, wobei der flüssige Olefinstrom in (b) mindestens überwiegend 1-Decen ist.
5. Verfahren nach einem der Ansprüche 1-4, wobei der Promotoranteil des in (a) thermisch gecrackten Komplexes ein Alkanol ist, das 1-8 Kohlenstoffatome enthält.
6. Verfahren nach einem der Ansprüche 1-5, wobei das Alkanol n-Butanol oder n-Propanol ist.
7. Verfahren nach einem der Ansprüche 1-6, wobei der Promotor in dem flüssigen Olefin in (b) derselbe Promotor wie der in dem thermisch gecrackten Komplex ist.
6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel l'alcanol est le n-butanol ou le n-propanol.
7. Procédé suivant l'une quelconque des revendications 1 à 6, dans lequel l'activateur dans l'oléfine liquide dans le point (b) est le même que l'activateur dans le complexe craqué thermiquement.

Revendications

1. Procédé de récupération de BF_3 à partir d'un courant de produits d'oligomérisation d'oléfines catalysée par un complexe BF_3 /activateur, lequel procédé comprend :
 - (a) le craquage thermique d'au moins une partie du complexe dans le courant de produits pour fournir du BF_3 gazeux, dans lequel ce craquage est conduit à une température inférieure à 80°C ;
 - (b) la mise en contact du BF_3 gazeux provenant de (a) avec un courant oléfinique liquide ayant une température comprise dans la gamme de 0 à 40°C , le courant oléfinique liquide contenant de $0,05$ à $1,5\%$ en poids d'activateur; et
 - (c) l'envoi du courant oléfinique résultant contenant le BF_3 dissous et le complexe BF_3 /activateur dans une unité de réacteur d'oligomérisation.
2. Procédé suivant la revendication 1, dans lequel le courant oléfinique dans (b) est choisi dans le groupe consistant en α -oléfine, oléfine interne ou mélange de celles-ci.
3. Procédé suivant la revendication 2, dans lequel l' α -oléfine contient 6 à 36 atomes de carbone et dans lequel l'oléfine interne contient 6 à 36 atomes de carbone.
4. Procédé suivant la revendication 1, dans lequel le courant oléfinique liquide dans (b) est au moins de façon prédominante du 1-décène.
5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel la partie activateur du complexe craqué thermiquement dans le point (a) est un alcanol contenant 1 à 8 atomes de carbone.

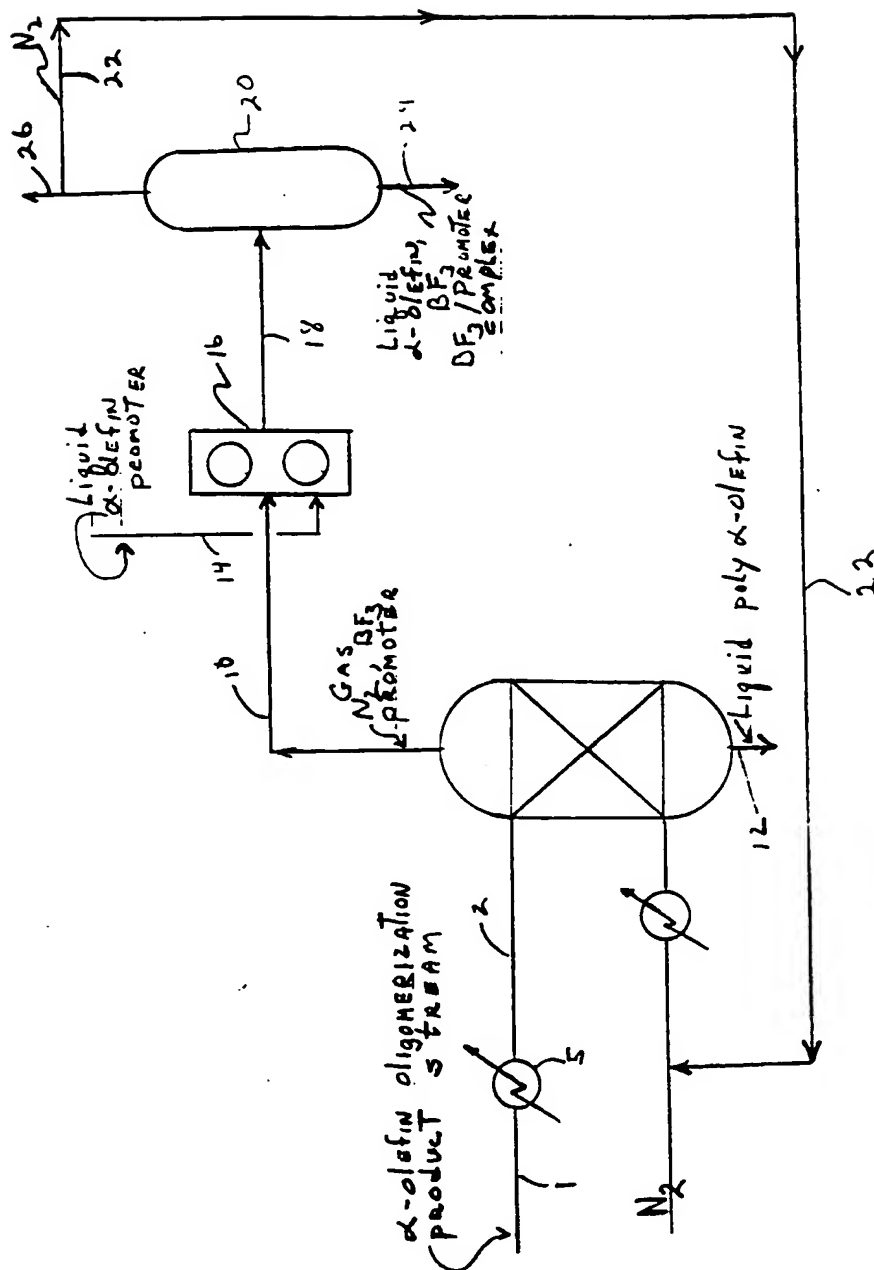


Figure 1